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(71) Applicant (for all treaty  
nations except the United  
States of America):

BAYER AKTIENGESELLSCHAFT [DE/DE]  
51368 Leverkusen, DE

(72) Inventor(s); and

(75) Inventor(s)/Applicant(s):  
(only for the US)

ZARGES, Wolfgang [DE/DE], Jakob-  
Böhme-Strasse 2, 51065 Cologne, DE.  
GROTH, Torsten [DE/DE], Bergstrasse  
52, 51519 Odenthal, DE. JOENTGEN,  
Winfried [DE/DE], Schlagbaumsweg 206,  
51067 Cologne, DE. GROSCHL, Andreas  
[DE/DE], Piet-Mondrian-Strasse 70,  
51375 Leverkusen, DE.

(74) Joint Representative:

BAYER AKTIENGESELLSCHAFT  
51368 Leverkusen, DE.

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(54) Title of the Invention:

PREVENTION AND DELAY OF DEPOSIT FORMATION IN MEMBRANE PROCESSES

(57) Abstract:

The invention relates to the use of polyaspartagine acids and their mixtures with tensides and emulgators in methods for carrying out membrane processes to inhibit or delay scale formation through hardly soluble organic and inorganic components in the membrane feed

## PREVENTION AND DELAY OF DEPOSIT FORMATION IN MEMBRANE PROCESSES

The invention pertains to the use of polyaspartic acids and mixtures of polyaspartic acids with surfactants and emulsifiers to prevent or delay the formation of deposits of sparingly soluble organic and inorganic components in the feed of membrane processes.

Membrane technology plays a significant role in the separation of fluidized systems. Established processes of the technology today include the production of drinking water from seawater by means of reverse osmosis and product reprocessing by means of ultrafiltration and nanofiltration.

What usually happens in membrane processes is that the concentration of dilute solutions is increased and organic solvents, water, or salt solutions are separated. As part of these processes, either valuable substances or harmful substances are obtained as concentrated solutions, which may possibly be low in salt. As a result, subsequent storage, transport, disposal, and further treatment can be conducted more cheaply. In cases of wastewater reprocessing, the goal of the membrane treatment is to obtain most of the volume as permeate in an untainted or only slightly tainted form so that it can be reused, for example. The concentrated retentate can be treated more easily to recover any valuable substances which it may still contain, or it can be disposed of more cheaply in this concentrated form by incineration, for example.

The area of membrane technology includes some very different processes, thus there are correspondingly different membranes and technical designs, e.g., membrane modules. Standard commercial membranes can consist of organic materials such as polysulfone, cellulose acetate, polyamide, or PVDF, or they can be made out of inorganic materials such as  $TiO_2$ ,  $ZrO_2$ , or  $Al_2O_3$ . Such membranes are used in the form of fine hollow fibers, tubes, or flat sheets.

The majority of membrane separation processes relevant to industry involve cross-flow filtration. High wall shear stresses, brought about by high flow rates and special module designs, are intended to minimize or prevent the contamination of the membrane. Nevertheless, fouling, i.e., the accumulation of material on the membrane, causes the output of permeate to decline in industrial membrane processes during which the concentration of the feed stream is being increased.

Scaling, i.e., encrustations of inorganic salts on the membrane when their solubility limit is exceeded, is a special case of fouling. The inorganic salts involved here are primarily the calcium and magnesium carbonates, hydroxides, phosphates, sulfates, and fluorides responsible for the hardness of water. During the reprocessing of wastewater, heavy metal hydroxides such as iron and chromium hydroxides represent an additional problem. Scaling is always to be expected when the goal of the process is to achieve high permeate outputs such as in the concentration of wastewater and in the production of pure water and drinking water. But it is also possible, of course, for this phenomenon to occur during desalination and the concentration of product solutions. The membrane processes considered here are ultrafiltration, nanofiltration, reverse osmosis, dialysis, and pervaporation.

Fouling, and scaling as a special case of fouling, ultimately cause the permeate output of a membrane system to fall to an uneconomically low level. From time to time, therefore, the feed stream must be shut off so that the membrane can be cleaned. This cleaning procedure, however, entails several disadvantages. Cleaning means that operations must be interrupted. Continuous operation can therefore be maintained only by shunting through another membrane system. Depending on the type of deposits, furthermore, it may be

necessary to use chemical cleaning agents, which frequently contain poorly biodegradable surfactants and chelating agents, and which must be disposed of separately. Finally, the cleaning procedure is almost never able to remove all of the deposits, so the membranes are seldom capable of their original permeate flow rate when they are put back into service.

If scaling is expected in the course of a process, pretreatment measures such as the use of ion-exchangers, which are known in the field of water softening, can be taken to prevent it. In certain scalant and module systems, furthermore, physical control of membrane encrustation in seeding and fluidized solids technologies can also be achieved by the intentional introduction of particulate solids (*Chem.-Eng.-Tech.*, Vol. 59, p. 187, 1987). Hydroxide accumulations can often be avoided by adjusting the pH to a suitable value. Nor has there been any lack of attempt to add chelating and sequestering agents such as NTA and EDTA to the feed stream to be processed. In addition to their undisputed disadvantageous ecotoxicological properties, however, chelating agents must be added in equimolar amounts. In contrast to chelating agents, dispersing agents, i.e., so-called threshold inhibitors, can be effective in preventing or delaying fouling and scaling in membrane processes in substoichiometric amounts.

In *Desalination*, Vol. 54, pp. 263-276, 1985, cited in *Chem. Abstracts*, Vol. 104, No. 56,102, polyphosphates, phosphonates, polystyrene sulfonates, polyacrylamides, and polyacrylates are being studied with respect to their scale-inhibiting action. US 5,256,303 describes how it is possible to prevent calcium sulfate from crystallizing and forming deposits in feed streams conducted through a membrane system. In this case, *N*-substituted polyacrylamides and phosphonobutane-1,2,4-tricarboxylic acid are used as scale inhibitors. EP

0,705,794 describes a method for preventing the crystallization of sulfates in aqueous systems. Here, one or more polyamino acids and one or more inorganic phosphates are used. To prevent the outfall water from undergoing eutrophication, however, these inhibitors must be disposed of, which is expensive. US 5,286,810 describes the production of high-molecular-weight polyaspartic acid copolymers, which also can be used as scale inhibitors in various industrial and hygienic areas. Reverse osmosis membranes are also mentioned, although no concrete details are offered. US 5,525,257 describes mixtures of polyaspartic acids and their derivatives with other polycarboxylic acids and their application in water treatments. Polycarboxylic acids such as polyacrylates, poly-maleates, and polysulfonates are mentioned. Here, too, reverse osmosis is mentioned but no details given. According to US 5,466,760, copolymers of polysuccinimide from maleic acid, ammonia, and a polyamine are used to inhibit salt deposits. EP-B 530,358 (= US 5,373,086) describes a special polyaspartic acid composition, which is obtained by heating L-aspartic acid in the form of a powder to at least 188°C, condensing it by further heating to at least 216°C until at least 80% of the polysuccinimide formation is completed, and then hydrolyzing the polysuccinimide, over 50% of which is in the  $\beta$ -form and which has a weight-average molecular weight of 1,000-5,000. This composition is used as an additive to inhibit the precipitation of  $\text{CaCO}_3$  or  $\text{Ca}_3(\text{PO}_4)_2$ . This special polyaspartic acid is said to be applicable over a wide industrial range from the treatment of water for industrial use to lubrication. Reverse osmosis is mentioned incidentally without any particular indications being given.

In summary it can therefore be said that, according to the present state of the art of membrane processes, phosphonates and polyacrylates have been

used as scale inhibitors. Polyaspartic acids are also listed in numerous publications as useful scale inhibitors. So far, however, no results have been forthcoming which document the applicability of polyaspartic acids in membrane processes. The expert knows that effective scale inhibition always depends on the overall system, i.e., on all of the participating components and conditions. In membrane processes in particular, however, there are many chemical and physical interference factors in play, meaning that a scale inhibitor that gives good results in some other area will not necessarily be all that effective specifically in membrane processes.

The surprising discovery has now been made that the formation of scale by sparingly soluble organic and inorganic components on membranes can be prevented and delayed in various types of membrane processes by the use of polyaspartic acids and mixtures of polyaspartic acids with surfactants and emulsifiers. The use of biodegradable polyaspartic acids is advantageous, because they can replace the phosphonates and polyacrylates, which are not biodegradable or only very slightly biodegradable, because they increase the availability of the membrane system, and because they reduce the number of cleaning steps.

The invention therefore pertains to a method for conducting membrane processes for the treatment of aqueous feeds containing inorganic and organic constituents during which the formation of scale on the membranes is prevented or delayed by the addition of a scale inhibitor, which is characterized in that polyaspartic acids and mixtures of polyaspartic acids with surfactants or emulsifiers or several of them [sic; with one or more surfactants or emulsifiers? -- Tr. Ed.] are used as scale inhibitors, where the polyaspartic acids are used in amounts of 1-50,000 ppm based on the amount of aqueous feed.

In a further elaboration, the invention pertains to the use of polyaspartic acids and mixtures of polyaspartic acids with surfactants and emulsifiers in the presence of polyacrylates or phosphonates such as phosphonobutane tricarboxylic acid or several such acids, because the use of polyaspartic acids improves the biodegradability of these mixtures.

The polyaspartic acids to be used in accordance with the invention can be produced in various ways. For example, they can be produced from maleic anhydride, water, and ammonia and/or from the secondary products derived from them such as maleic acid-NH<sub>4</sub> salt, maleamic acid, aspartic acid, asparagine, and iminodisuccinic acid. It is also possible to use their ammonium salts.

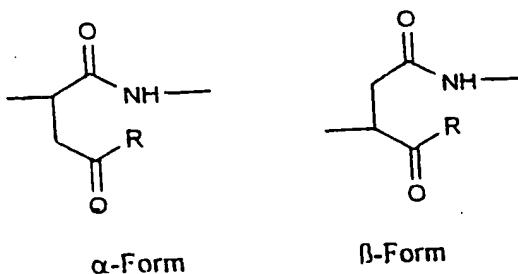
Mixtures in which all of the above-cited components are present simultaneously can also be used to produce polyaspartic acids. The acids can also be produced thermally from the previously cited components in the presence of acid catalysts such as phosphoric acid, phosphonic acids, sulfonic acids, or sulfuric acid, which promote the formation of peptide bonds.

The polyaspartic acids or polysuccinimides resulting initially from the condensation reaction are usually subjected to solvolysis or hydrolysis, preferably to alkaline hydrolysis, possibly in the presence of amines such as ethanolamines or alcohols such as ethylene glycol or propanetriol. The polyaspartic acids thus obtained are preferably used in the form of their salts to prevent and delay scale formation. Examples of the production of the polyaspartic acids to be used according to the invention can be found in the following literature sources. In *J. Org. Chem.*, Vol. 26, p. 1,084, 1961, polyaspartic acid is produced by the thermal condensation of aspartic acid. In US 4,839,461, maleic acid and ammonia are reacted at 120-150°C. In US 5,288,783, maleic acid and fumaric acid are reacted with ammonia at 170-350°C. In US

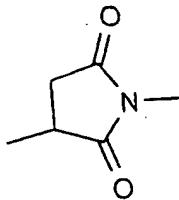
5,493,004, polyaspartic acids are formed by the reaction of malic anhydride and ammonia in a tubular reactor. The resulting product can be subjected to further polymerization if desired in a very-viscous-flow reactor. Common to all these production methods is that the polysuccinimides which are formed first are then subjected to solvolysis or hydrolysis, preferably alkaline hydrolysis. It is also possible, however, to use amines, amino alcohols, and alcohols to form derivatives.

The polyaspartic acids to be used according to the invention can contain varying amounts of the following structural elements, depending on the production method used:

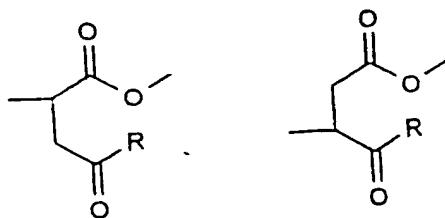
(a) aspartic acid units:



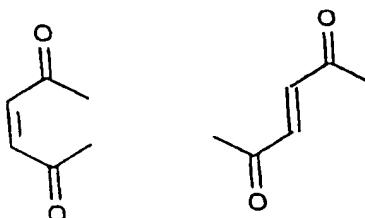
(b) succinimide units:



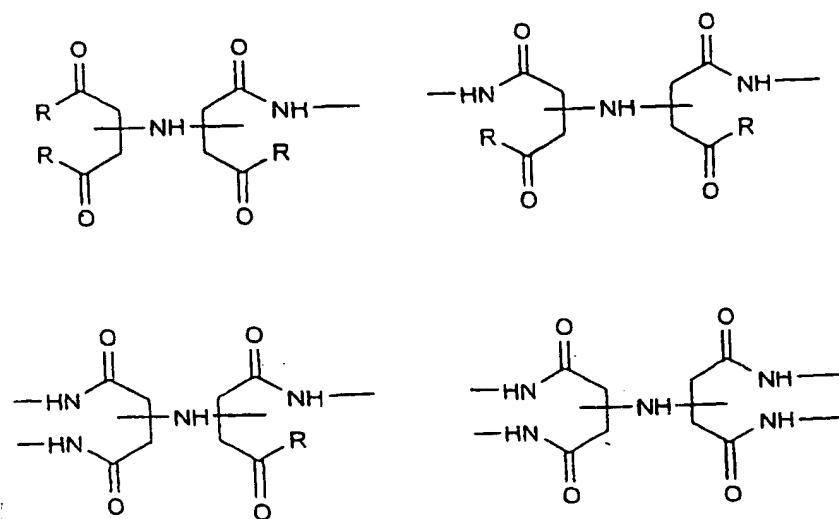
(c) malic acid units:



(d) olefinic units:



(e) iminodisuccinic acid units:



In all the structural elements shown above, R = OH, ONa, OLi, OK, ONH<sub>4</sub>, NH<sub>2</sub>, OH<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>OH, OH<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>, OHN(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub>, or OCH<sub>2</sub>CH<sub>2</sub>OH.

The molecular weight of the polyaspartic acids to be used according to the invention, i.e., the weight-average molecular weight as determined by GPC (gel permeation chromatography), can be 500-50,000, preferably 1,000-20,000, and even more preferably 1,500-10,000.

The structural elements are determined qualitatively and quantitatively

by NMR and FT-IR spectroscopy, mass spectrometry, HPLC, GC, and elementary analysis. The peptide bonds can be present in the  $\alpha$ -form and the  $\beta$ -form. In general, the polyaspartic acids represent an  $\alpha/\beta$  mixture, in which the amount of the  $\beta$ -form is larger than the amount of the  $\alpha$ -form.

According to the invention, the polyaspartic acids can be used in combination with a surfactant, especially an emulsifier. Anionic, cationic, non-ionic, and amphoteric surfactants (emulsifiers) are suitable. Examples which can be mentioned include the anionic alkylsulfonates and the nonionic polyglycol ethers (alkoxylates). It is preferable to use linear alkylsulfonates and the polyglycol ethers of aliphatic alcohols. It is even more preferable to use linear  $C_{12}$ - $C_{17}$ -alkylsulfonates and unsaturated and/or saturated aliphatic  $C_{10}$ - $C_{20}$ -alcohols which have been etherified with 6-60 ethylene oxide units.

The mixtures of polyaspartic acids and possibly surfactants, especially emulsifiers, are formulated in such a way that they fulfill the task of scale inhibition and scale prevention. If the deposits are formed primarily by inorganic and organic salts of alkaline-earth ions and heavy metal ions, then primarily polyaspartic acids will be used. To the extent that the deposits are formed by nonpolar organic substances, more of the surfactant (emulsifier) will be used. The quantitative ratio of polyaspartic acids to surfactants and/or emulsifiers can be adjusted as a function of the fouling and scaling in the membrane process. The weight ratio of polyaspartic acids to surfactants and/or emulsifiers can therefore be in the range of 100:0 to 1:99, preferably in the range of 100:0 to 10:90, and most preferably in the range of 100:0 to 50:50.

Either alone or in their mixtures with surfactants (emulsifiers), the polyaspartic acids can be used in combination with polyacrylates and phospho-

nates. As a result, the biodegradability of the resulting active ingredient mixtures is increased in comparison with the biodegradability of the polyacrylates and phosphonates without preventing the deposit-preventing effect.

Polyaspartic acids and their mixtures with surfactants (emulsifiers) are used in membrane processes at pH values of 3-12.5, preferably of 4.5-11, and even more preferably of 6-10. Insofar as the pH value is not determined by the feed stream being used in the membrane process, any desired acids and bases can be used to adjust the pH; acids and bases which do not form sparingly soluble salts with other constituents of the feed are preferred. The selected acids and bases should not, however, exert any damaging effect on the constituents of the feed stream, on the metal materials, or on the membranes themselves.

Polyaspartic acids and their mixtures with surfactants, especially emulsifiers, are used in membrane processes at a temperature of 10-90°C, preferably of 15-70°C, and even more preferably of 20-50°C.

The membranes used in the membrane processes can consist of inorganic materials such as ceramic,  $TiO_2$ ,  $ZrO_2$ , or  $Al_2O_3$ ; or they can consist of organic polymers such as cellulose esters (cellulose acetate, cellulose acetobutyrate, cellulose acetopropionate), polyamides, polyimides, polyesters, polyethersulfone, polyetherketone, polysulfone, or PVDF. The process according to the invention is preferably applied to nanofiltration and ultrafiltration membranes made of the materials cited. It is also preferable for the process according to the invention to be applied to reverse osmosis membranes with a selective separation layer of polyamide. It is especially preferable for the selective separation layer for membranes in all the processes cited to consist of a polyamide. All of the membranes used in the process according to

the invention are asymmetric or of the thin-film composite type known to the expert.

Polyaspartic acids and their mixtures with surfactants, especially emulsifiers, can be used to prevent and delay the formation of scale on membranes in membrane processes which are supplied with aqueous and solvent-containing aqueous feed streams. In general, the feed streams must be of such a kind that the active ingredients are initially in solution and as a result are able to perform their intended function. So that the optimum effect is achieved, the compounds/salts responsible for the scaling/fouling should also be in solution initially and not exceed their solubility limit until after the membrane process has begun. Examples of feeds which can be treated according to the invention include seawater, landfill percolation water, industrial and domestic sewage, and product streams with scaling potential.

Polyaspartic acids and their mixtures with surfactants (emulsifiers) are added to the feed stream to be treated in a membrane system in amounts of 1-50,000 ppm, preferably in amounts of 5-5,000 ppm, more preferably in amounts of 10-500 ppm, and most preferably in an amount of 50-500 ppm.

#### EXAMPLES

##### Example 1

A Lab 20 plate module was equipped with 1 each of the following plates (= 2 flat membranes): an ultrafiltration membrane, a nanofiltration membrane, and a reverse osmosis membrane, all from Desalination Systems, USA. First, the permeate output for completely desalinated water was determined at 25°C under a module feed pressure of 20 bars. Next, polyaspartic acid (= PAA; molecular weight about 6,000) was added in two different concentrations to the feed. The effects on permeate output were observed.

### Results

Amount of PAA Added	Permeate Flux Densities, L/(m <sup>2</sup> · d)		
	UF Membrane	NF Membrane	RO Membrane
0 ppm	1,200	2,330	800
50 ppm	1,200	2,330	800
500 ppm	1,150	2,430	880

### Example 2

(a) 200 L of a solution produced from completely demineralized water and 2.0 g/L of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  was first concentrated by 50% with a nanofiltration membrane (sulfate retained > 95%) in a spiral-wound type of module (2.5" x 40", 47 mil spacer) (conditions: 25°C, 30 bars module outlet pressure, 1.25 m<sup>3</sup>/h flow rate to the module). The permeate output was measured several times in a closed-loop system, that is, with the recirculation of retentate and permeate to the feed.

(b) Experiment (a) was repeated after the addition of 50 ppm of PAA (molecular weight 6,000).

(c) Experiment (a) was repeated after the addition of 50 ppm of PAA (molecular weight 6,000) and 1% NaCl. After 3 h in the closed-loop system, the concentration was increased even further, to the extent that the  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  concentration of the feed was approximately 14 g/L.

### Result

Without any addition, the crystallization of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (solubility in  $\text{H}_2\text{O}$  at 25°C, 2.9 g/L) interrupted the permeate flux. With PAA, supersaturation by a factor of 4.5 could be realized without any loss of permeate output.

The addition of electrolytes did not interfere either.

Results of Example 2

The permeate flux density in  $\text{L}/(\text{m}^2 \cdot \text{day})$  as a function of time under the conditions of Examples 2a, 2b, and 2c and the obtainable  $\text{CaSO}_4$  concentration:

TABLE. KEY: (a) time, min; (b) permeate flux density, Example . . . . ,  $\text{L}/(\text{m}^2 \cdot \text{d})$ ; and (c)  $\text{CaSO}_4$  concentration, g/L.

Zeit [min] (a)	Permeatflußdichte Beispiel 2a [ $\text{L}/(\text{m}^2 \cdot \text{d})$ ] (b)	Permeatflußdichte Beispiel 2b [ $\text{L}/(\text{m}^2 \cdot \text{d})$ ] (b)	Permeatflußdichte Beispiel 2c [ $\text{L}/(\text{m}^2 \cdot \text{d})$ ] (b)	Konzentration $\text{CaSO}_4$ [g/L] (c)
0	2793	2700	2592	ca. 2,0
5	2793	2700	2592	ca. 2,5
10	2793	2700	2592	ca. 3,0
15	2793	2700	2592	ca. 4,0
45	432	2120	2140	ca. 4,0
75	295	2120	2140	ca. 4,0
105	216	2120	2140	ca. 4,0
135	180	2120	2140	ca. 4,0
165	162	2120	2140	ca. 4,0
195	149	2120	2140	ca. 4,0
225	139	2120	2140	ca. 4,0
230		2120	2314	ca. 5,0
235		2120	2314	ca. 7,5
240		2120	2250	ca. 14
270			2160	ca. 14
300			2160	ca. 14
330			2160	ca. 14
360			2160	ca. 14

Figure 1 is a graphic illustration of the table.

Example 3

Sodium bicarbonate fluidized with calcium phosphate was used in the synthesis of a sulfo group-containing stilbene brightener. The synthesis salt still present (NaCl) was removed from the product solution, which contained  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{CaCO}_3$ , NaCl, and the brightener as the main constituents, by using nanofiltration tubular membranes (1.2 m module, 1/2") and the product solution was concentrated to approximately 55% of the original volume (flow rate to the module 1  $\text{m}^3/\text{h}$ ; 55°C; feed pressure 25 bars). The calcium content increased from 70 mg/L to 140 mg/L in the final concentrate. The solubility limit of  $\text{Ca}_3(\text{PO}_4)_2$  of 20 mg/L was clearly exceeded. After the addition of 100 ppm of PAA, the same permeate outputs were obtained as those obtained when processing product solution that contained no  $\text{Ca}_3(\text{PO}_4)_2$ , that is, with a solution produced without any fluidized sodium bicarbonate (permeate flux densities of 2,300  $\text{L}/(\text{m}^2 \cdot \text{day})$  during diafiltration; 1,000  $\text{L}/(\text{m}^2 \cdot \text{day})$  during concentration). After the experiment, the original permeate output could be restored by rinsing with water.

Example 4

500 mL of a solution containing 3 mmoles of calcium chloride was added to 500 mL of a solution containing 1 mmole of sodium carbonate, 1 mmole of sodium sulfate, and 1 mmole of sodium fluoride. The resulting solution was supersaturated by a factor of 4.5 with  $\text{CaF}_2$  and by a factor of 7 with respect to  $\text{CaCO}_3$ . A voluminous precipitate formed rapidly at pH > 8; at pH 5, a fine-crystalline precipitate formed after a certain delay. No precipitates formed after the addition of 50 ppm of PAA (molecular weight 6,000).

### Example 5

A sulfuric acid mother liquor from dye production was neutralized by the addition of milk of lime before membrane system reprocessing. After the neutralization sediment had been separated, the solution, which was now saturated with calcium sulfate, was concentrated by means of nanofiltration membranes in a spiral-wound type of module (2.5" x 40", 47 mil, 30 bars module feed pressure, 25°C, flow rate to the module = 1,250 L/h). The following experiments were compared:

- (a) The permeate flux was measured during concentration to 20% of the starting volume and in a subsequent closed-loop system.
- (b) 50 ppm of a mixture of PAA and polyacrylic acid (3:1) was added to the feed.

### Result

The permeate outputs in Experiment 5b were significantly higher during concentration and closed-loop operation than they were without the addition.

### Results of Example 5

Permeate flux density in L/(m<sup>2</sup>· day) as a function of time under the conditions of Example 5a and 5b and the obtainable CaSO<sub>4</sub> concentrations [see table on following page -- Tr. Ed.].

TABLE. KEY: (a) time, min; (b) permeate flux density, Example . . .  
 L/(m<sup>2</sup>·d); and (c) CaSO<sub>4</sub> concentration, g/L.

(a) Zeit [min]	Permeatflußdichte Beispiel 5a (b) [l/(m <sup>2</sup> ·d)]	Permeatflußdichte Beispiel 5b (b) [l/(m <sup>2</sup> ·d)]	Konzentration CaSO <sub>4</sub> (c) [g/l]
0	1371	1371	ca. 3,0
10	1143	1231	ca. 3,5
20	1032	1116	ca. 4,0
30	1000	1032	ca. 5,0
40	889	980	ca. 6,0
50	788	914	ca. 8,5
60	667	873	ca. 14,5
90	320	762	ca. 14,5
120	267	632	ca. 14,5
150	202	600	ca. 14,5
180	145	600	ca. 14,5
210	121	565	ca. 14,5
240	114	533	ca. 14,5

Figure 2 is a graphic illustration of the table.

CLAIM(S)

1. Method for implementing membrane processes for the treatment of aqueous feeds containing inorganic and organic constituents in which the formation of scale on the membranes is prevented or delayed by the addition of a scale inhibitor, characterized in that polyaspartic acids and mixtures of polyaspartic acids with surfactants, especially emulsifiers, are used as scale inhibitors, where the polyaspartic acids are used in amounts of 1-50,000 ppm based on the amount of aqueous feed.

2. Method according to Claim 1, characterized in that polyaspartic acids and mixtures of polyaspartic acids with surfactants, preferably emulsifiers, are used in the presence of polyacrylates or phosphonates or a mixture of these.

3. Method according to Claim 1, characterized in that polyaspartic acids are used which have a weight-average molecular weight of 500-50,000, preferably of 1,000-20,000, and even more preferably of 1,500-10,000, as determined by gel permeation chromatography [= size-exclusion chromatography -- Tr. Ed.].

4. Method according to Claim 1, characterized in that polyaspartic acids are used which are produced from maleic anhydride and ammonia in the presence of water or from their secondary products such as maleic acid-NH<sub>4</sub> salt, maleamic acid, aspartic acid, asparagine, and the ammonium salts of maleic acid, maleamic acid, aspartic acid, asparagine, and iminodisuccinic acid, or their mixtures, by thermal condensation, possibly in the presence of acid catalysts to obtain polysuccinimides, followed by solvolysis or hydrolysis to obtain, for example, polyaspartic acid salts.

5. Method according to Claim 4, characterized in that the polyaspartic

acids are used in the form of their sodium salts.

6. Method according to Claim 1, characterized in that the surfactants, preferably emulsifiers, which can be used in the mixture with polyaspartic acids are selected from a group consisting of anionic, cationic, nonionic, and amphoteric surfactants and emulsifiers, preferably alkylsulfonates and the alkoxylates, and even more preferably linear  $C_{12}$ - $C_{17}$ -alkylsulfonates and polyethers based on unsaturated and/or saturated  $C_{10}$ - $C_{20}$ -alkanols and [sic; "etherified with" -- Tr. Ed.] 6-60 ethylene oxide units.

7. Method according to Claim 1, characterized in that the membrane processes are conducted at a pH of 3-12.5, preferably of 4.5-11, and even more preferably of 6-10.

8. Method according to Claim 1, characterized in that the polyaspartic acids and the totality of the surfactants and/or emulsifiers are used in a weight ratio of 100:0 to 1:99.

9. Method according to Claim 1, characterized in that the membranes are used as nanofiltration or ultrafiltration membranes.

10. Method according to Claim 1, characterized in that reverse osmosis membranes with a selective separation layer of polyamide are used.

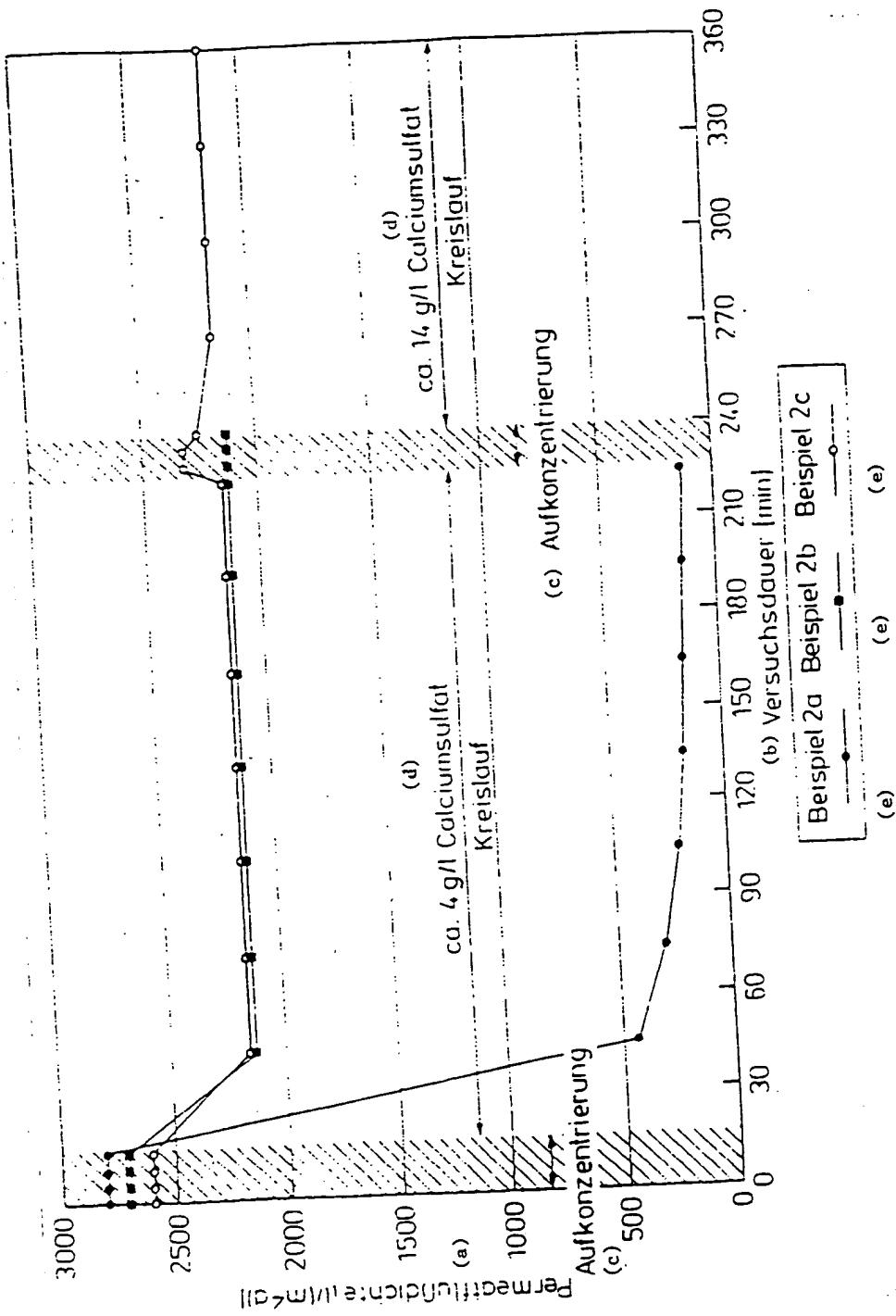


Figure 1. KEY: (a) permeate flux density,  $L/(m^2 \cdot d)$ ; (b) duration of experiment, min; (c) incr asse in concentration; (d) calcium sulfate concentration ca. .... g/L, closed-loop system; and (e) Example ....

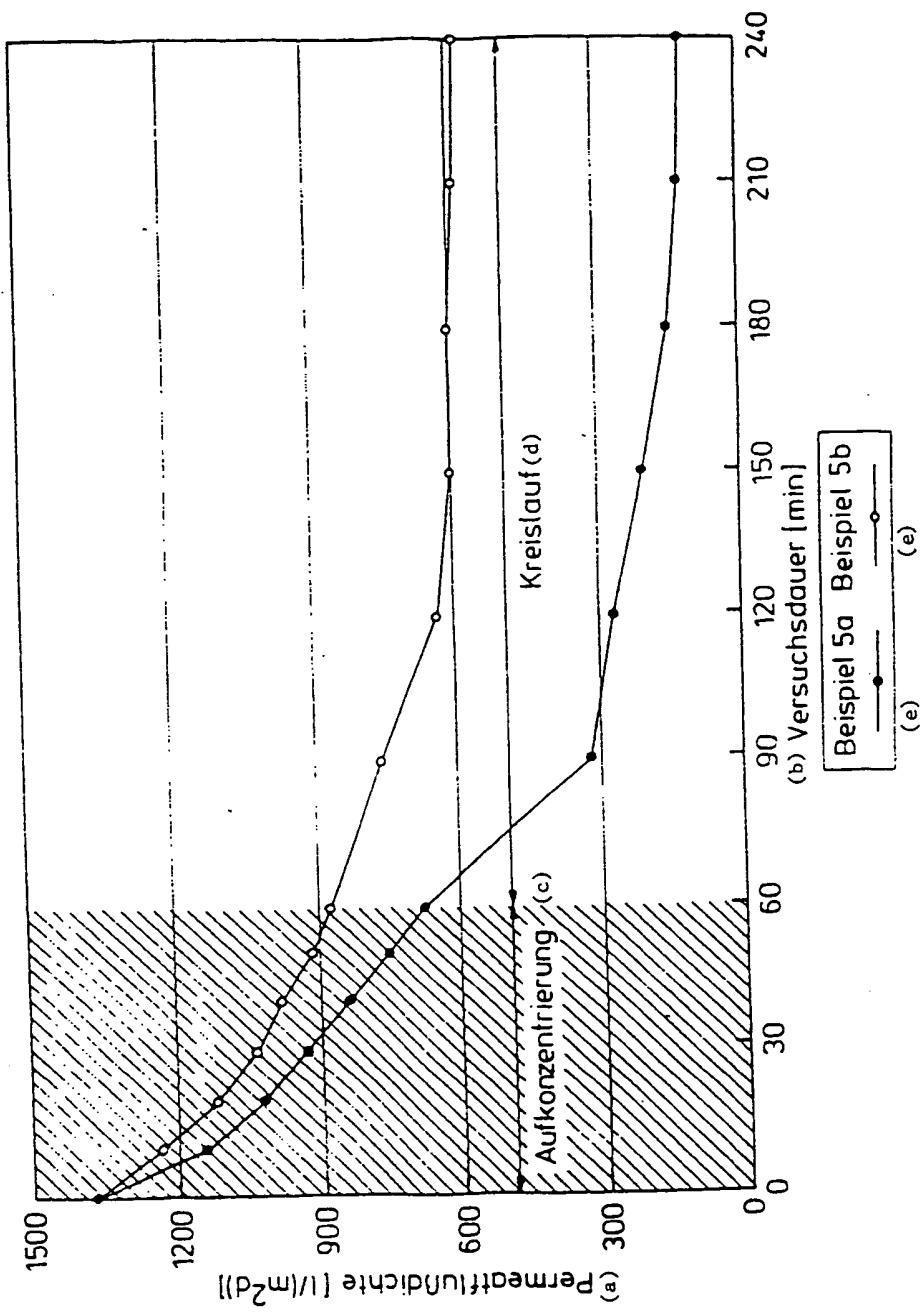


Figure 2. (a) permeate flux density,  $L/(m^2 \cdot \text{day})$ ; (b) duration of experiment, min; (c) increase in concentration; (d) closed-loop system; and (e) Example ....